

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

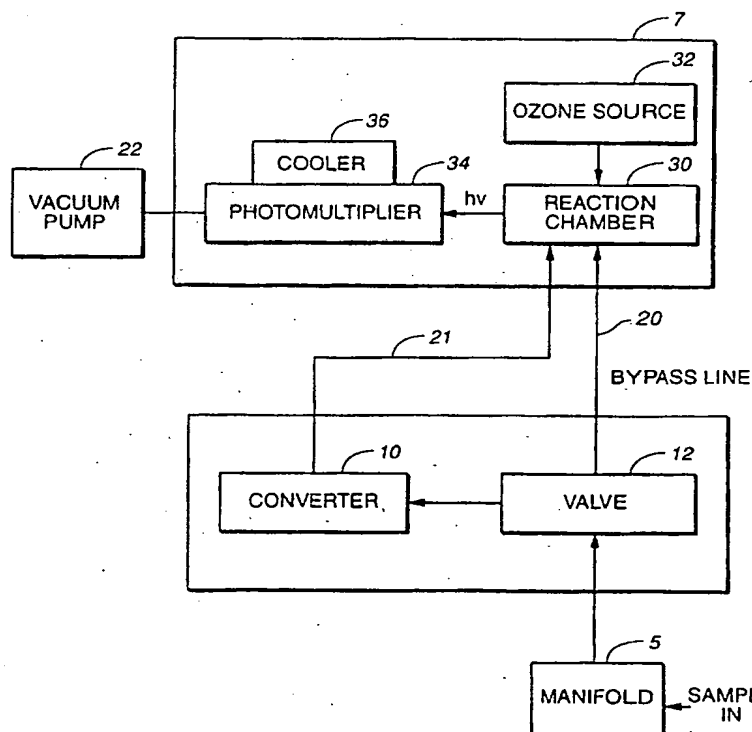
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : G01N 33/00, 21/76		A1	(11) International Publication Number: WO 98/38508
		(43) International Publication Date: 3 September 1998 (03.09.98)	
(21) International Application Number: PCT/US98/03998		(81) Designated States: JP, KR, SG, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(22) International Filing Date: 27 February 1998 (27.02.98)		Published <i>With international search report.</i>	
(30) Priority Data: 08/795,949 28 February 1997 (28.02.97) US 08/996,790 23 December 1997 (23.12.97) US			
(71) Applicant: EXTRACTION SYSTEMS, INC. [US/US]; 10 Forge Park, Franklin, MA 02038 (US).			
(72) Inventors: KISHKOVICH, Oleg, P.; 45 Austin Avenue, Greenville, RI 02828 (US). KINKEAD, Devon, A.; 86 Briarcliff Lane, Holliston, MA 01746 (US).			
(74) Agents: WILLIAMS, John, N. et al.; Fish & Richardson P.C., 225 Franklin Street, Boston, MA 02110 (US).			

(54) Title: SYSTEM FOR DETECTING AMINE AND OTHER BASIC MOLECULAR CONTAMINATION IN A GAS

(57) Abstract

The detection system is constructed to examine multiple amines in gas to produce a reading that is stoichiometrically related to the proton bonding characteristic of the multiple amines present in the sampled gas. In one aspect, the detection system includes at least two channels through which gas samples to be examined pass, at least one convertor (6) for converting the multiple amines into NO, and at least one chemiluminescent NO detector (7) for producing signals representative of the NO concentration in air passing therethrough. In another aspect, the detection system includes at least two channels through which gas samples to be examined pass, an amine remover (120), which has a high removal efficiency for both strong and weak amines, coupled to one of the channels.



AP2

- 1 -

SYSTEM FOR DETECTING AMINE AND OTHER BASIC MOLECULAR CONTAMINATION IN A GAS

5

Background of the Invention

The invention relates to the detection of base contaminants in air, especially amine contaminants, and to systems employing such detection, including semiconductor fabrication systems and systems for
10 filtering air for semiconductor fabrication and other processes that require uncontaminated air of high quality.

A particular purpose of the invention is to reliably measure low concentrations of airborne base
15 contaminants in a semiconductor manufacturing environment that may adversely affect base-sensitive photolithographic processes being employed.

In semiconductor manufacturing it has been found desirable to detect an organic amine such as NMP (normal
20 methyl pyrrolidinone) or ammonia. Such a contaminant may interfere for instance with a photolithography process used in semiconductor fabrication. The base contaminant may react with protons produced as a result of exposure of a photoresist layer to light. This can interfere with
25 proper exposure and can harm the yield of the process and the rate of production of the semiconductor wafers.

For this reason, semiconductor manufacturers have sought to measure and control the concentration of airborne molecular contamination during the critical
30 steps of the photolithography process which are sensitive to it. A detecting instrument specific to the detection of NMP and a detecting instrument specific to the detection of ammonia have been employed in semiconductor

- 3 -

ammonia, semiconductor manufacturers have used chemical filters to remove the contaminants. These filtering systems employ filter stages within an enclosure, the filter media of each stage being penetrable by air with acceptable pressure drop. As air flows through the filtering system, unwanted contaminants are retained on the chemically active surface of the various stages of the filter system. A problem associated with such filtering systems has been to accurately predict the remaining life of the filter so that the filter media can be changed at appropriate times with minimal disruption to the use of the expensive production facility. In the case of semiconductor fabrication facilities, typically, filter life has been estimated by measuring the concentration of ammonia in the air flow associated with the filter system.

Summary of the Invention

The measurement of ammonia only is not satisfactory to photolithographic processes that are affected by low concentration of any basic material or amines, such as chemically amplified DUV photoresist processing. The measurement of total fixed nitrogen species is not applicable because many of the species (e.g., HCN, NO, NO₂) are not basic in nature and do not affect the process. Detection of ammonia at high concentrations is not useful for the monitoring of amines at low levels.

None of the techniques mentioned above have suggested the concept of the present invention of measuring in a single, non-specific reading, the concentration at low levels of the multiple amines in air exposed to photolithographic processes and the like, that will be described more fully below.

- 5 -

to produce a reading stoichiometrically related to the proton bonding characteristic of the multiple amines present, the detection system comprising at least two channels through which gas samples to be examined pass, 5 at least one convertor for converting the multiple amines into NO, and at least one chemiluminescent NO detector for producing signals representative of the NO concentration in air passing therethrough, wherein the total amine concentration is determined based upon the 10 difference between the detected NO concentration in a converted gas sample and the detected NO concentration in an unconverted gas sample.

In another aspect, the invention features a detection system for detecting base contamination at low 15 concentrations in gas characterized in that the detection system is constructed to examine multiple amines in gas to produce a reading stoichiometrically related to the proton bonding characteristic of the multiple amines present, the detection system comprising at least two 20 channels through which gas samples to be examined pass, an amines remover, which has a high removal efficiency for both strong and weak amines, coupled to one of the channels, a convertor for converting the multiple amines into NO, and at least one chemiluminescent NO detector 25 for producing signals representative of the NO concentration in air passing therethrough, wherein the total amine concentration is determined from the difference between the detected NO concentration in a converted gas sample that has passed through the amines 30 remover and the detected NO concentration in a converted gas sample that has bypassed the amines remover.

In yet another aspect, the invention features a detection system for monitoring molecular amine

- 7 -

the difference between the determined NO concentrations in the target air sample and in the reference air sample.

In still another aspect, the invention features a method of monitoring molecular amine contamination in sampled air, comprising: providing a reference air sample; providing a target air sample; converting amines in the target air sample into NO; determining by chemiluminescence, under pressure conditions of 150 millibar or lower, the NO concentrations in the reference air sample and in the target air sample; and determining a total amine contamination concentration from the difference between the determined NO concentrations in the target air sample and in the reference air sample.

The invention also features a method of monitoring molecular amine contamination in sampled air, comprising: sampling air from a region; delivering sampled air to a scrubber having a high removal efficiency for both strong and weak amines; delivering scrubbed air sample to a converter for converting amines therein to NO to provide a reference air sample; delivering sampled air to a converter for converting amines therein NO to provide a target air sample; determining by chemiluminescence the NO concentrations in the reference air sample and in the target air sample; and determining a total amine concentration from the difference between the determined NO concentrations in the target air sample and in the reference air sample.

Other features and advantages will become apparent from the following description and from the claims.

Brief Description of the Drawings

Fig. 1 is a plan view of a deep UV photolithography processing facility employing a contaminant detection system.

- 9 -

is a diagrammatic view of three converters coupled together in series. Fig. 12e is a diagrammatic view of a detection system that includes three separate sample channels coupled to an NO detector.

5 Fig. 13 is a diagrammatic view of a sample delivery train similar to that of Fig. 12 in which an isolation valve is located upstream of an amine scrubber.

Fig. 14 is a diagrammatic view of a sample delivery train similar to Fig. 13 in which the pressure
10 reducer is located downstream of a thermal catalytic converter.

Fig. 15 is a diagrammatic view of a sample delivery train similar to Fig. 13 in which the pressure reducer is located downstream of an amine scrubber and a
15 selection valve.

Fig. 16 is a view similar to Fig. 12 of a system implemented to be immune to variations in NO_x at the sampling site.

Fig. 17 is a flowchart of a process for
20 determining the optimum sample cost and sample frequency.

Fig. 18 is a table illustrating the operation of the process of Fig. 17.

Fig. 19 is a flowchart of a process for determining the sample sequence based on past
25 performance.

Fig. 20 is a flowchart of a process for determining the sample sequence based on average concentrations.

Description of the Preferred Embodiments

30 In Figure 1 a photolithography tool cluster for the production of semiconductor wafers is shown. The cluster consists of two tools, a stepper 8, and a track

- 11 -

either alone, or in-series in the make-up or recirculation air system of the cleanroom.

As shown in Fig. 2, each filtration tower, 1 and 1a, includes, respectively, an upstream sampling port 2, 2', a downstream sampling port 4, 4', and an intermediate sampling port 3, 3'. Sampling ports 8a and 9a are likewise provided for the stepper 8 and track 9, respectively. For each filter and tool combination, there is one converter, 6 (for the stepper 8) and 6' (for the track 9). These two converters, 6 and 6', are connected to a common, remotely located NO_x detector, 7. The detector, for instance, may be a Model 17 detector available from Thermo Environmental Instruments Inc.; the converters may be obtained from Thermo Environmental Instruments, Inc. The converters 5, 5' are preferably located near the sampling sites to obtain rapid stabilization of determination cycle and, consequently, rapid accurate readings to give early warning of any contaminant problems. Amine contaminants have a high adsorption coefficient relative to the interior surfaces of typical sampling lines, and deposits of amines in long sample lines can require long periods of flushing until a stable reading is obtained. On the other hand, the converted gas, NO, has a low adsorption coefficient relative to the sample line surfaces. Thus, by localizing the NO converter at the site to be monitored, only a short sample line is subject to adsorption of amines, while the extended line between the converter and the remote detector conducts air containing relatively non-adsorptive NO. In this manner, the sampling cycle can be of very short duration, to provide early warning for the detection of unwanted contaminants.

- 13 -

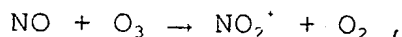
equivalent NO value. This value is stoichiometrically related to the aggregate proton-bonding characteristic of all the amines present in the sample.

In addition to the detection of total amines, by
5 suitable adaptations, NO and NO₂ concentrations in the unfiltered air are readily determined by the detector as well. For certain applications, it is desirable to know the NO and NO₂ present.

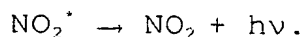
In another embodiment, an impinger 23 is employed
10 to identify possible contaminants in the unconverted sample air, as shown in Fig. 3. The impinger consists of a glass or quartz tube holding a liquid. In this embodiment, vacuum pump 22 and an associated calibrated flow controller are employed to draw sample air through
15 the liquid to take a grab sample. The grab sample is then analyzed or subjected to real-time colorimetric analysis, providing a quantitative assessment of the amine contaminants in the sample air.

Referring to Fig. 4, a filtration tower 1 is shown
20 with a corresponding computer controlled manifold 5 and converter 6. The sampling manifold, 5, directs the specified sample to the converter while it directs a respective unconverted sample directly to the detector. Two sampling lines 20, 21 thus extend to the detector,
25 for distances as long as, for example, 1000 feet. The length of the sampling lines is not critical because, as previously mentioned, the converted gas, NO, has a low adsorption coefficient relative to the interior surface of sampling lines, constructed, for example, of PTFE
30 (TEFLON™ brand of PTFE available from DuPont) and stainless steel, whereas, in the case of the sample inlet gas, no measurement of amines is made so deposits in the sample lines are of no consequence.

- 15 -



where the ozone is provided by an internal ozone generator 32. This produces electronically excited NO_2 molecules which in returning to the ground state emit 5 photons, $h\nu$, that are detected by appropriately cooled photomultiplier 34. The reaction is given by the expression



Associated electronics amplifies the signal from the 10 photomultiplier (PMT) to provide a reading of NO_x concentration.

The ozone reaction is conducted under conditions that prevent conversion of amines to NO , so that the NO_x reading of the sample arriving unconverted from the 15 sample port $\text{NO}_x(u)$ is not disturbed either by amines in the air sample or amines adhered to the inner surfaces of the sample conduit. Total amine detection, A_T , is then determined by comparison of the reading for the unconverted sample $\text{NO}_x(u)$ with the reading $\text{NO}_x(c)$ for the 20 converted sample according to the expression

$$\text{NO}_x(u) - \text{NO}_x(c) = \Delta\text{NO}_x = A_T .$$

To achieve the needed sensitivity for current deep UV photolithographic processes with presently available photomultipliers, the photomultiplier tube is cooled at 25 least to -5°C . To achieve sensitivities required for next generation fine resolution deep UV photolithography in semiconductor manufacturing, the tube is cooled to -15°C by associated thermoelectric cooler 36. Moreover,

- 17 -

substantially free of amine contamination) is provided by filter system 1 for the stepper subsystem and by filter system 1a for the track subsystem. By having the converter near the sampling area, the length of the sampling lines exposed to amines is reduced, which increases the response time of the system.

To calibrate each converter-detector subsystem, two or more samples of known concentration of contaminants are provided to the instrument, as illustrated in Fig. 7. The instrument response is then compared with the known concentrations, and a calibration curve is generated and either manually or electronically, through the software, associated with the instrument to provide corrections to the instrument's response. In general, the instrument response over the concentration range remains stable for an extended period. The instrument is sensitive to zero calibration, and for reasons such as drift of the PMT the curve must be shifted relative to the true zero reading as it varies over time. Because in photolithography processing harmful contaminant concentrations are extremely low (on the order of 1 ppb or lower), in preferred systems the zero calibration is performed regularly (at least once a day) to assure the fidelity of the zero reading. In a particular preferred implementation, the detection system is arranged to operate continuously, as shown in Fig. 8, whereby the system performs a total amine detection for each of the sampling ports in turn, and conducting two calibrations each cycle, one with respect to each of the converters with which the detector operates.

In the preferred embodiment, the zero air employed for calibration is provided by the outlet ports 4 (and 4') of the filtration system (see Fig. 1). The instrument

- 19 -

the stepper or track exceed a predetermined threshold, an alarm is enabled and the process is immediately shut down. However, by use of this detection system, the occurrence of such an emergency can normally be avoided.

5 As shown in Fig. 9, the filtering system is continuously monitored in real time as follows. The sample at the inlet to the filter system, over time, provides a quantitative history of the input of amines or other Bronstead base contaminants to the filter. By use
10 of samples drawn from the intermediate position along the filter system as well as from the outlet of the filter stack, and measuring the difference in concentration levels from these locations, one of the following steps is caused to occur: if the difference is zero (condition
15 green) and the total amine or Bronstead base concentration at the tool is within operating limits, then the operation continues with no interruption; when the difference is greater than zero, the difference is compared with a predetermined threshold; if the threshold
20 is not exceeded (condition yellow), operation continues but a filter replacement is scheduled; if the threshold is exceeded, or if the total amine detected at the tool exceeds operating limits (condition red) the operation is immediately shut down.

25 Another way of predicting the time for filter replacement employs the total amine detector to detect total amines from a sample port upstream of the filtering system. This provides information regarding the past
30 history of contaminant concentration in the airflow that has passed through the filtering system. The contamination of air entering the system may change because of the season of the year, industrial or agricultural activity in the region, or accidental spills

- 21 -

areas of contamination leaks. By following an escalating amine concentration trend, the mobile unit localizes the source of the contamination.

As illustrated in Fig. 11, the invention, in
5 another preferred embodiment, is combined with a multi-point sampling system of an array of sensors to monitor the operating status of a track, including temperature, temperature of the hot plate, time on the chill plate, exposure time, etc. A total amine detector monitors
10 process contaminants in air such as the concentration of an adhesion promoter, such as hexamethyldisilozane (HMDS), during the coating stage where photoresist is applied to the semiconductor wafers. The wafers are then sent to the stepper for exposure and subsequently brought
15 back to the track for developing. During this stage, another, or the same, total amine detector monitors the concentration of another possibly internally processed chemical contaminant, such as
tetramethylammoniumhydroxide (TMAH), employed in the
20 developing stage.

The present invention enables, in its total amine reading, the simultaneous detection of NMP and ammonia, typically monitored previously with separate detectors. The invention enables detection, in its total amine
25 reading of other amines that are known to be harmful to the photolithography process, such as morpholine, diethylamine ethanol, and cyclohexylamine, agents which are commonly used to inhibit corrosion in high humidity regions. Amines from the facility cafeteria, especially
30 seafood, are also included in the detection as well as amines from the breath of the facility workers, that can create high levels of amine contamination, depending upon diet and smoking habits. As has been explained, the

- 23 -

ambient NO or NO₂ level occur, then the fidelity of the total measurement would be compromised and large variations in ambient NO or NO₂ level could make the signal so noisy that the data is not useful.

5 According to the present invention accurate chemiluminescent detection of total amines at low concentrations, for protection of the base-sensitive processes, is achievable.

10 The following further embodiments are particularly effective in this regard. These embodiments use an amine or process-specific (e.g., photoresist-coated) removal device or scrubber to provide, in one channel, a reference sample for non-specifically measuring "total amines" from a second channel from the same source. By
15 removing from the reference sample substantially all of the molecules corresponding to the class of amines of interest, the reference sample may be used as a baseline for canceling the effects of background, nitrogen-containing contaminants which might contribute to the NO
20 concentration detected by the chemiluminescent detector in the target air sample. Also, it has been determined that amine detection sensitivity improves as the operating pressure of the chemiluminescent NO
25 concentration measurement decreases. Accordingly, the chemiluminescent NO detection is preferably carried out at sub-atmospheric pressures of 150 millibar absolute, 125 millibar absolute, or less to achieve a low noise levels and to achieve a detection sensitivity of 1 part per billion (ppb), preferably 0.5 ppb, or better.

30 Referring to Fig. 12, in this preferred embodiment, a sample delivery train 110 is shown for determining the total amine concentration in a sample of gas using an internal reference for zero air (i.e., amine-

- 25 -

contrast, commonly-used tubing of PTFE is relatively porous and tends to emit hydrogen fluoride, a strong acid, which reacts with ammonia and amines, interfering with the measurement of total amines. Silica may be deposited onto the stainless steel tubing using chemical vapor deposition. Glass tubing, steel tubing, and fiberglass tubing may also be coated with silica to reduce sample line contamination. Silica-coated sample lines 116 are used throughout sample delivery train 110 to convey the gas sample from sampling ports 112 to chemiluminescent detector 126. In certain applications, sample lines comprising glass are used; the glass sample lines may be coated with silica. The glass sampling lines may be reinforced with epoxy.

In certain advantageous embodiments, sample lines 116 are heated substantially along their total length to approximately 50°C using electrical heating lines (see, e.g., U.S. Patent 3,727,029, incorporated herein by reference). This reduces the tendency for amines to deposit on the walls of the tubing (reduces amine-sticking coefficient) and thus reduces sample line contamination of the alternating sample gas slugs.

In this context, the combination of heating the sample lines with use of a silica coating on the lines is advantageous, though heating of sampling lines of other composition, by itself, can provide a beneficial effect. Heating is preferably accomplished using electrical resistance wire incorporated in the wall of the sample line or otherwise disposed in heat transfer relation to it.

Selection valve 114 (e.g. multi-position valve manufactured by Vici) enables samples from different locations to be channeled into a single sample delivery

- 27 -

valve 123a is equivalent to the pressure drop between pressure reducer 118b and three-way valve 123b.

The split of the gas into channels A and B occurs after the sample exits pressure reducer 118. A three-way valve 122a may be used to direct the sample into channels A and B. The amine scrubber 120 of channel A is constructed to selectively remove from the sample the totality of the multiple bases or amines to which a photolithographic or other process being guarded is sensitive, but it is constructed to not affect other nitrogen-containing compounds. Amine scrubber 120 is preferably a solid-state scrubber, comprised of an ion exchange resin with active sulfonic or carboxylic groups. The scrubber may also be comprised of any material that preferentially binds the airborne molecular bases (e.g. photoresist-coated substrates, weak acid-coated substrates, strong acid-coated substrates, ion exchange materials, or chemically treated activated carbon and molecular sieves). The properties of the active media can be chosen to optimize the selectivity of the detection process. The scrubber can be a chemical air filter medium, along the lines of the air filter that supply "zero air" in the previously described embodiments 1-10. In other embodiments of the broad aspects of the invention, the scrubber can be a wet scrubber.

A strong cation exchange resin is preferred as the scrubber substance in scrubber 120 of Fig. 12. The resin within amine scrubber 120, being a strong acid, removes multiple molecular bases, such as ammonia and other amines, and thereby enables total amines detection. A strong cation exchange resin that has a high amines removal efficiency (e.g., a removal efficiency of about 100% for all amines of interest) ensures the removal of

- 29 -

section scrubber, for detecting the particular amines against which a respective process is being guarded.

Three-way valve 122 of Fig. 12 allows the amine-free sample from channel A and the unscrubbed sample from channel B to be directed to thermal catalytic converter 124 alternately, in rapid sequence. Operating the delivery train at 125 millibar pressure, for example, enables three-way valve 122 to switch between channel A and channel B several times per minute, to enable averaging of a number of readings, if desired, within a short monitoring interval, for instance ten minutes or less.

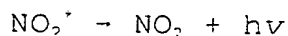
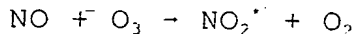
Thermal catalytic converter 124 (e.g., as manufactured by Thermo Environmental Instruments Inc.) converts amines in each gas sample to nitrogen oxide (NO) by thermal oxygenation. Since any given sample from channel B may contain a variety of amines (such as morpholine, diethylamine ethanol, NH_3 , and normal methyl pyrrolidinone) thermal catalytic converter 124 must have high conversion efficiency for many types of amines. To achieve high conversion efficiency (85-100%) for a broad range of amines, a stainless steel (304 grade) surface heated to 900°C is used within thermal catalytic converter 124. The gas sample becomes oxygenated as it passes over the heated stainless steel surface resulting in the conversion of amines to NO.

A suitable catalytic converter is diagrammatically illustrated in Fig. 12c. The converter is comprised of a reaction chamber 150 that may or may not contain a catalytic element 152 (e.g., platinum and/or palladium), a heating element 154 to heat the reaction chamber, and a thermocouple 156 connected to power control relay 158 which regulates the temperature of the reaction chamber.

- 31 -

manufactured by Thermo Environmental Instruments Inc.). The detector 126 employs chemiluminescence for NO detection. Typically, maximum signal from chemiluminescence detector 126 is achieved at a pressure of about 65 Torr and a flow rate of 1.5 about liters per minute under the operating conditions described above. Detector 126 operates at approximately 125 millibar, suitable for detection of low amine concentrations. This high sensitivity affords detection of total amine concentrations of less than 1 ppb, preferably less than 0.5 ppb.

In the detector, NO is caused to react with ozone to produce electronically excited NO₂ molecules (NO₂^{*}) which in returning to ground state emit photons, hv, that are detected by a photomultiplier.



The signal from the photomultiplier is converted into time-based NO concentration values by a control system 130 and then the total amine concentration of the gas sample from the selected sampling point is determined, e.g. by appropriate averaging and differencing the values. The total amine concentration for the gas sample equals the difference between the NO concentration of the unscrubbed sample from channel B, e.g., at time t₁ (or the average of NO concentrations determined at times t₁ + t₃ + ...t_{n-1}, n being an even number) and the NO concentration of the amine-free sample from channel A, e.g., at time t₂ (or the average of NO concentrations determined at times t₂ + t₄ ...+t_n, n being an even number).

Additional channels may be used to provide further analysis of the components of the sampled air. For example, referring to Fig. 12e, three channels (CH1, CH2

- 33 -

average calculation may be represented by the following algorithm.

Moving NO Average = $(X_1 + X_2 + \dots + X_n) / n$,
where X equals the NO concentration at a given time and n
5 equals the total number of NO measurements made. The
moving average calculation may be reset periodically to
avoid the weighting of out-of-date measurements. In
another algorithm, a selected number of values are added
together to provide an initial average value and
10 thereafter the oldest value is dropped from the average
as the newest measured value is added to it.

Control system 130 (e.g., a computer), in addition
to collecting and analyzing data received from
chemiluminescence detector 126, also controls selection
15 valve 114 and three-way valve 122. Selection valve 114
is controlled by control system 130 to channel samples
from multiple sampling ports 112 into the sample delivery
train 110 in a selected order. Three-way valve 122 is
controlled to switch between channel A and channel B on
20 the basis of settling times. Preferably, multiple
switching cycles are employed for a given sample line and
the measurements are averaged, or a running average is
employed, to produce a reliable measure of total amines,
as has been described.

25 As shown in dashed lines, for some applications a
further conduit 116a may be connected to valve 122,
communicating with an auxiliary vacuum pump 128a and
valve 122 is modified to connect the non-selected channel
A or B to the auxiliary pump. In this way substantially
30 steady state flow conditions can be maintained in the
amine scrubber, and fresh sample is immediately available
to the converter 124 upon actuation of valve 122.

- 35 -

zero air by directing a sample to amine scrubber 120 and then to a thermal catalytic converter 124a and a chemiluminescence detector 126a. At the same time, channel 2 directs a sample to a thermal catalytic converter 124b and a chemiluminescence detector 126b. The NO measurements from channel 1 and 2 are made simultaneously and then compared. This embodiment eliminates the effect of fluctuations in ambient NO and NO₂ concentrations by determining the actual NO and NO₂ concentration at the same time as the total NO response is being measured.

Control system 130' calculates the total amine concentration based on the differences between the two readings from detectors 126a and 126b. A calibration system (not shown) is employed to compatibly zero the instruments (e.g., to accommodate variations in the converters and detectors) so they can operate together. A correction factor based upon, e.g., computer look up of an experience table, can be employed. A calibration routine can be conducted periodically, and drift trends can be measured and stored to create a dynamic correction algorithm.

This arrangement eliminates the possibility of noise from variations in ambient NO and NO₂ concentrations because the instantaneous value of the NO and NO₂ concentration is always known and does not change during a calculation cycle. This system, in effect, reduces the time between ambient NO and NO₂ measurements to zero, which solves the fundamental problem of fluctuations in NO and NO₂ concentrations during a single calculation cycle.

The various embodiments may be implemented in a number of useful ways. The parameters of the amine

- 37 -

when scanning the array of values, determines the location of an amine leak (e.g., in a semiconductor process) by providing an automatic direction finder. In this case the mobile monitoring station may be
5 automatically directed and controlled by the search algorithms to find amine leaks.

For controlling the sampling frequency of multiple sample locations in a monitoring system, an actuarial algorithm is advantageously used. On the basis of sample
10 cost, the sampling frequencies for the various sampling points are determined in the manner that the points of greatest sensitivity and importance are monitored with greatest frequency.

In Fig. 17, a flowchart 170 of a system that
15 performs this function is shown. The data input steps for the monitoring system include entering at step 172 the average cost of an alarm event at each sampling port 112 (i.e., the cost associated with exceeding a predetermined total amine concentration at the respective
20 location), at step 174 or 174a the alarm event frequency (i.e., how frequently a sample taken from a particular sampling point will exceed a predetermined level), and at step 176 the capital costs and operating costs for the monitoring system (i.e., present value of capital and
25 operating costs for sampling). Initially, these inputs are entered either from a database or are manually entered by a user using an input device such as a keypad connected to a computer. For instance, an alarm frequency is entered at 174a as determined by the
30 software program by reference to the recorded history of alarm events at each sampling point.

Based upon the inputs, the system performs two initial calculations. At step 180, the actuarial

- 39 -

for manually changing sample frequency in accordance with the determination of the program. An optimum sampling frequency for each sampling port is calculated according to the following formula:

5 Optimum sampling frequency = (optimum sample
 cost/hr)(equipment sample frequency/actual
 equipment cost),

where the equipment sample frequency equals the number of samples the monitoring system can process per hour
10 divided by the number of sampling ports. Fig. 18 is a table providing examples of the calculations previously mentioned for a hypothetical monitoring system using seven sampling locations.

Referring to Fig. 19, in another embodiment, a
15 flowchart 203 of a system that optimizes sample frequency based upon past performance is shown. At step 201 the concentration history at each sampling location 112 is entered into the memory of a multi-channel base
contaminant monitor 200. Step 202 calculates and records
20 the frequency with which a given sampling location exceeds a predetermined level. The frequency data for each sampling location then become inputs 204 into optimum sample frequency calculation step 206. The sample sequencing is adjusted at step 208 in accordance
25 with stored optimization criteria data which, for example, is weighted according to the cost of alarm events at the respective sampling locations. The monitor is also structured to determine a sampling sequence for new channels which have similar characteristics to the
30 existing channels. The sample frequency optimization improves monitoring efficiency by adjusting sample frequency based upon empirical evidence.

- 41 -

1. A detection system for detecting base contamination at low concentrations in gas characterized in that the detection system is constructed to examine multiple amines in gas to produce a reading
5 stoichiometrically related to the proton bonding characteristic of the multiple amines present, the detection system comprising at least two channels through which gas samples to be examined pass, at least one convertor for converting the multiple amines into NO, and
10 at least one chemiluminescent NO detector for producing signals representative of the NO concentration in air passing therethrough, wherein the total amine concentration is determined based upon the difference between the detected NO concentration in a converted gas
15 sample and the detected NO concentration in an unconverted gas sample.

2. A detection system for detecting base contamination at low concentrations in gas characterized in that the detection system is constructed to examine
20 multiple amines in gas to produce a reading stoichiometrically related to the proton bonding characteristic of the multiple amines present, the detection system comprising at least two channels through which gas samples to be examined pass, an amines remover,
25 which has a high removal efficiency for both strong and weak amines, coupled to one of the channels, a convertor for converting the multiple amines into NO, and at least one chemiluminescent NO detector for producing signals representative of the NO concentration in air passing
30 therethrough, wherein the total amine concentration is determined from the difference between the detected NO concentration in a converted gas sample that has passed through the amines remover and the detected NO

- 43 -

pressure drop in the channel with the amine remover is equivalent to the pressure drop in the other channel.

11. The detection system of claim 2 whereby the amines remover is constructed to remove only multiple
5 amines of interest from air passing through one of the channels.

12. The system of claim 11 combined with a photoresist system for conducting a process which is particularly sensitive to a limited class of multiple
10 amines, wherein the amines remover is constructed to selectively remove the limited class of amines to which the process is particularly sensitive.

13. The detection system of claim 1 or 2 wherein the channels comprise glass tubing.

14. The detection system of claim 13 wherein the
15 glass tubing is coated with silica.

15. The detection system of claim 13 in which the glass tubing is heatable substantially along its total length to reduce amine deposition on the walls of the
20 tubing.

16. The detection system of claim 13 in which the glass tubing is reinforced with epoxy.

17. The detection system of claim 2 further comprising a control system operable to implement a
25 process for lowering the amplitude of intra calculation cycle concentration variations of NO and NO₂.

18. The detection system of claim 17 in which the process is based on a moving average selected to smooth the noise in the measurement in a manner that diminishes
30 over-time as the number of averaging cycles increases.

19. The detection system of claim 17 in which the control system is operable to implement an actuarial process that controls the sampling frequency of multiple

- 45 -

a first air channel for delivering a reference air sample;

a second air channel for delivering a target air sample;

- 5 a converter coupled to the second air channel for converting molecular amine contamination in the target air sample into NO;

a chemiluminescent NO detection system coupled to the first and second air channels for determining the NO
10 concentrations in the reference air sample and in the target air sample; and

a pressure reducing system coupled to the chemiluminescent NO detector for reducing operating pressure of the chemiluminescent NO detector to a level
15 of 150 millibar or lower;

wherein a total amine contaminant concentration in the sampled air may be determined from the difference between the determined NO concentrations in the target air sample and in the reference air sample.

- 20 26. The detection system of claim 25 wherein the pressure reducing system comprises a flow restrictor.

27. The detection system of claim 30 wherein the first and second air channels have respective characteristic flow diameters, and the pressure reducing system
25 comprises a pressure reducer located upstream of the chemiluminescent NO detector and having an air channel with a characteristic flow diameter that is smaller than the characteristic flow diameters of the first and second air channels.

- 30 28. The detection system of claim 27 further comprising a vacuum pump located downstream of the chemiluminescent NO detector.

- 47 -

between the determined NO concentrations in the target air sample and in the reference air sample.

32. The detection system of claim 31 wherein the tubes defining the first and second air channels each
5 comprises an interior silica surface exposed for contact with air flowing therethrough.

33. The detection system of claim 31 wherein the first and second air channels are each formed from glass tubes reinforced with epoxy.

10 34. A method of monitoring molecular amine contamination in sampled air, comprising:
providing a reference air sample;
providing a target air sample;
converting amines in the target air sample into

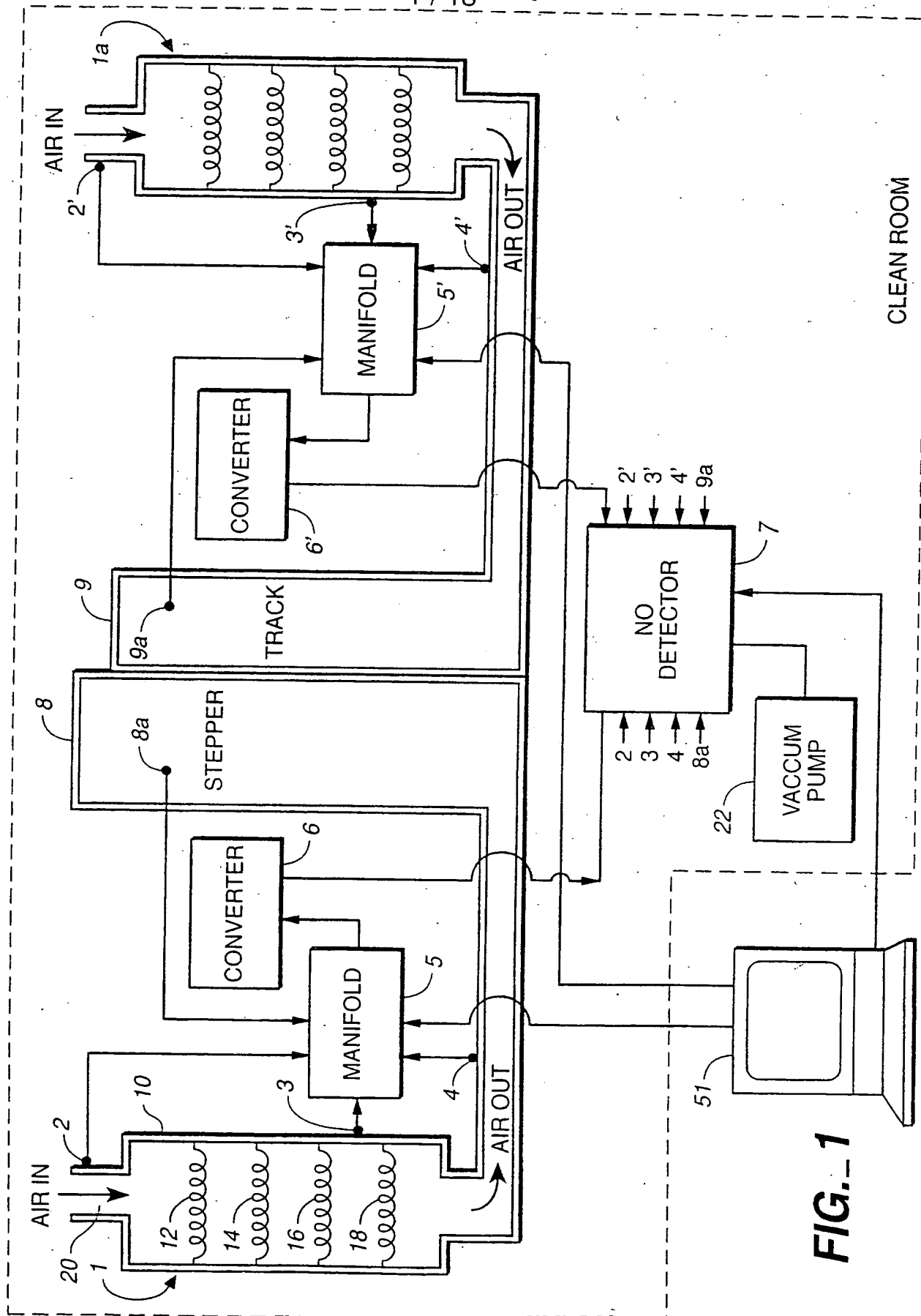
15 NO;
determining by chemiluminescence, under pressure conditions of 150 millibar or lower, the NO concentrations in the reference air sample and in the target air sample;

20 determining a total amine contamination concentration from the difference between the determined NO concentrations in the target air sample and in the reference air sample.

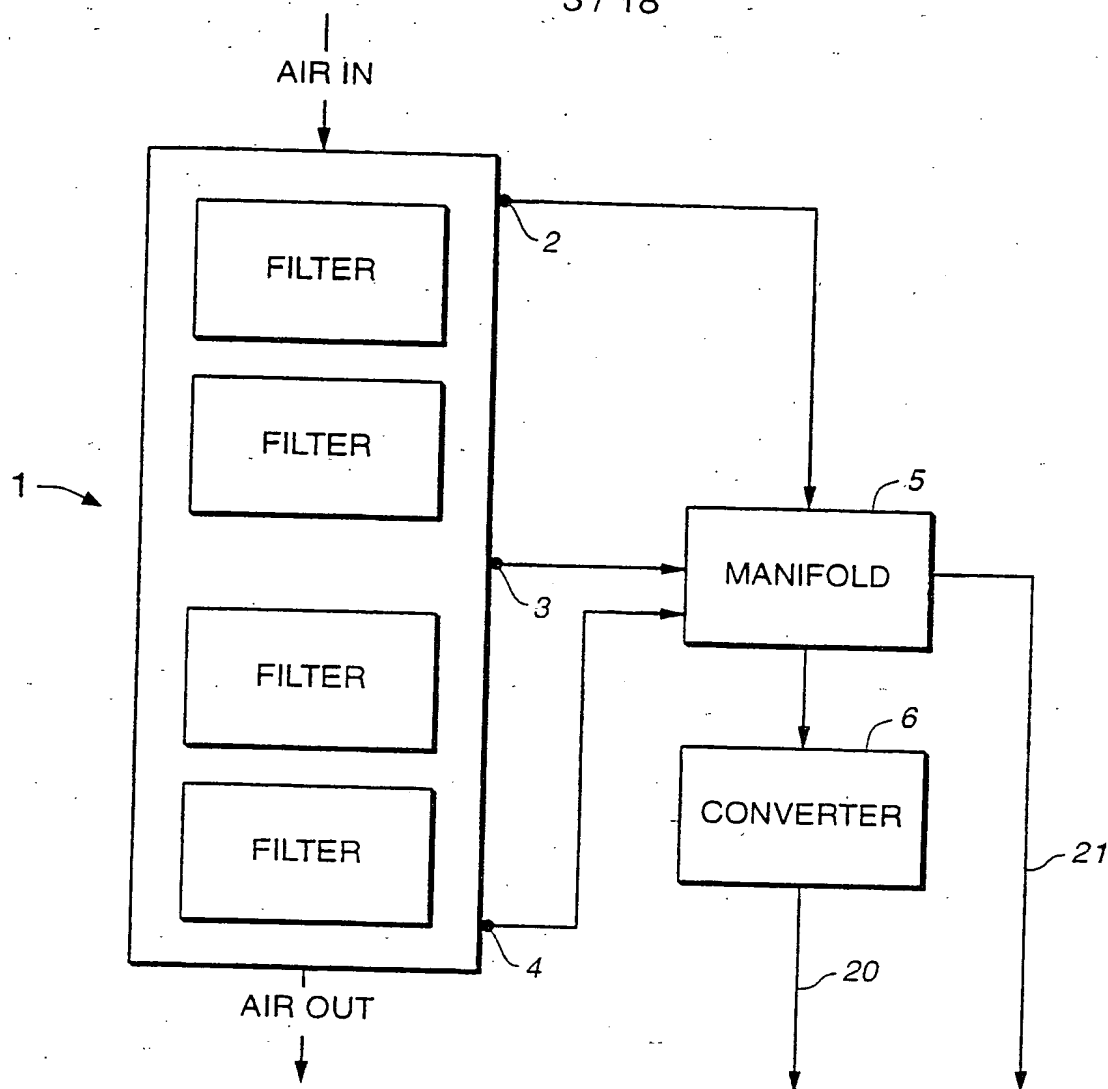
25 35. The method of claim 34 wherein the NO concentrations in the reference air sample and in the target air sample are determined by chemiluminescence at a pressure of 125 millibar or less.

30 36. A method of monitoring molecular amine contamination in sampled air, comprising:
sampling air from a region;
delivering sampled air to a scrubber having a high removal efficiency for both strong and weak amines;

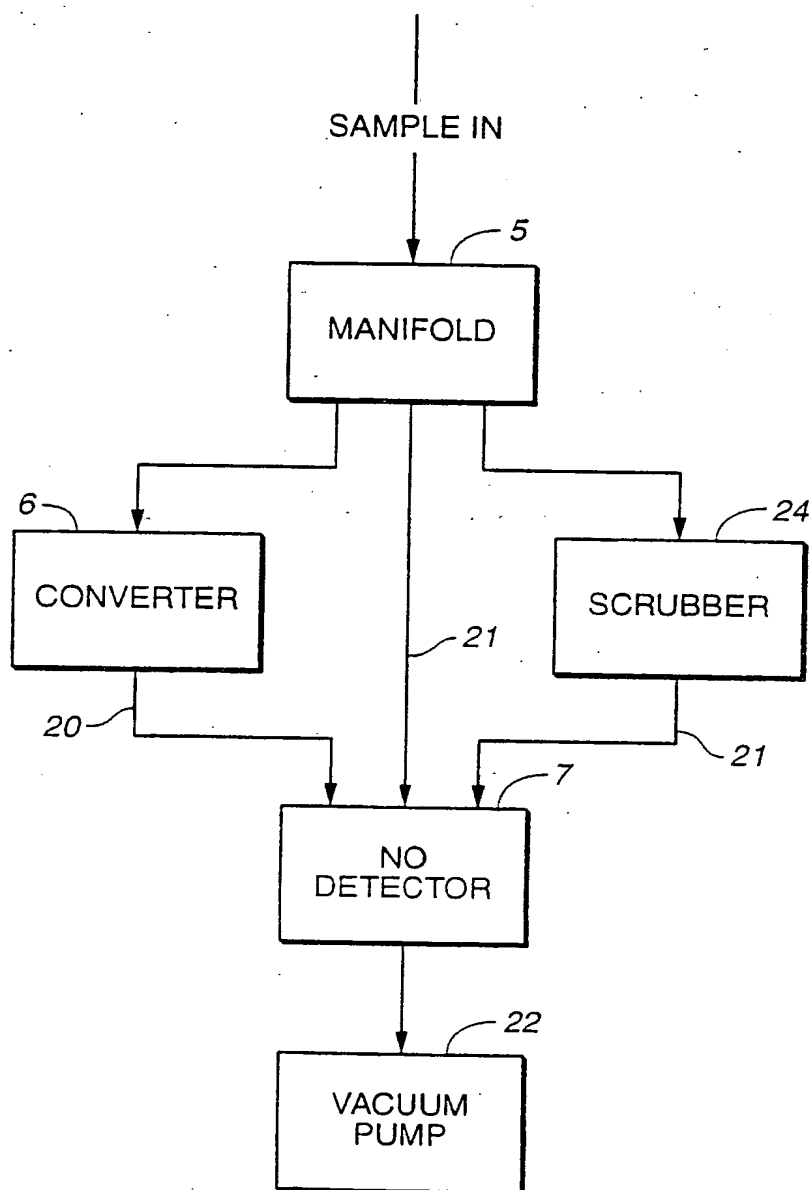
1 / 18



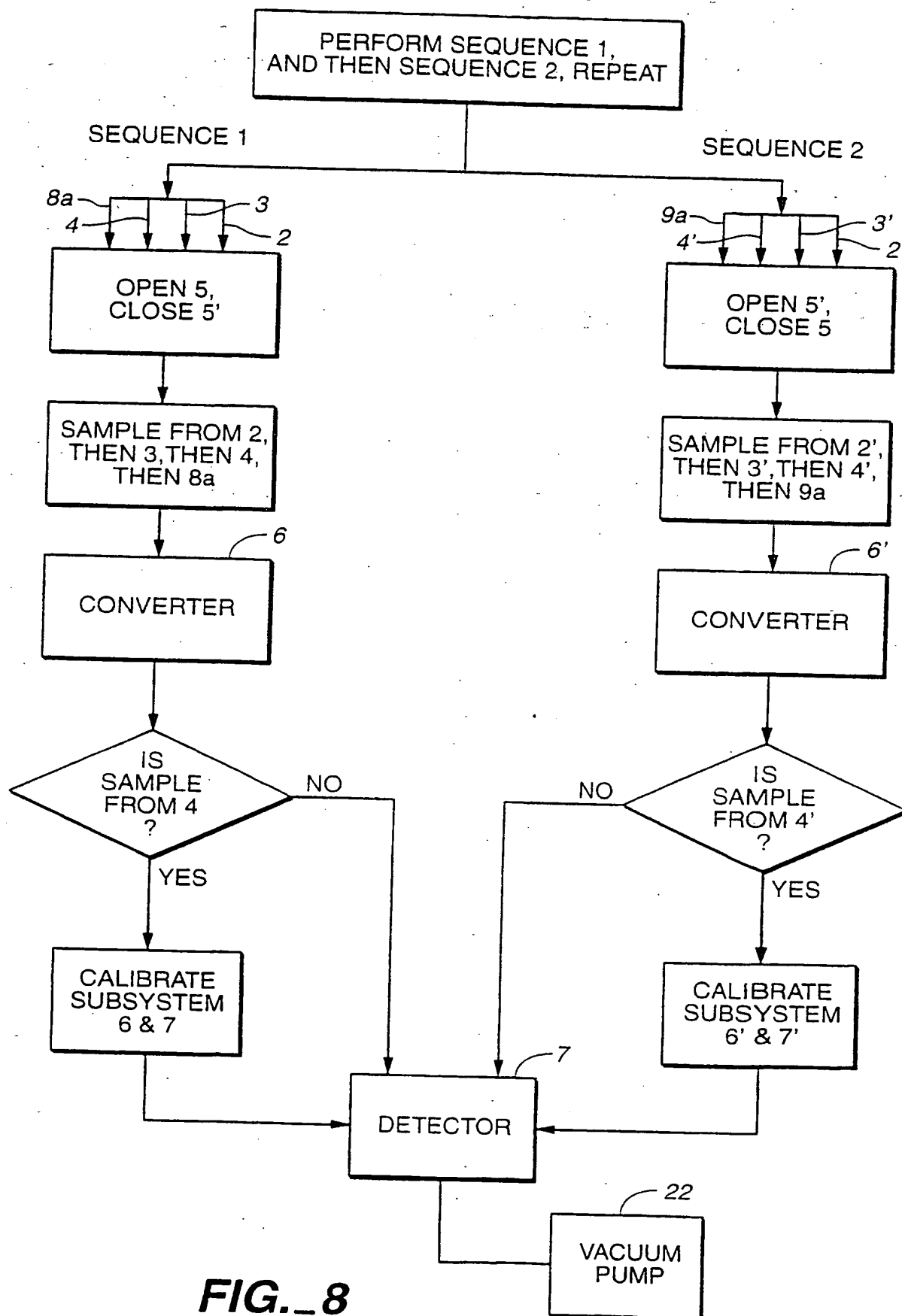
3 / 18

**FIG. 4**

5 / 18

**FIG. 6**

7 / 18

**FIG. 8**

9/18

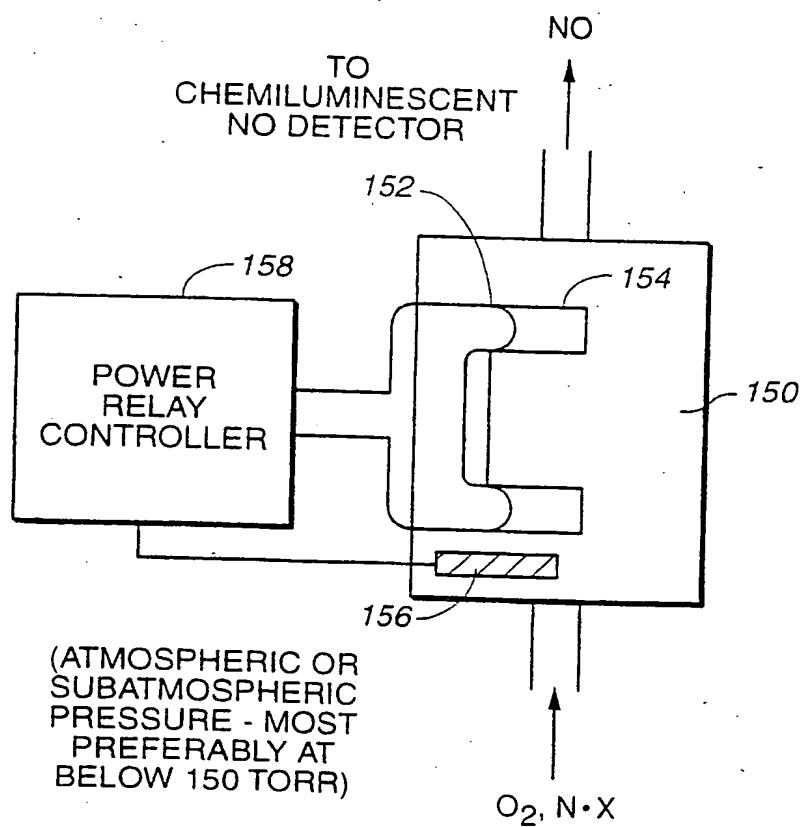
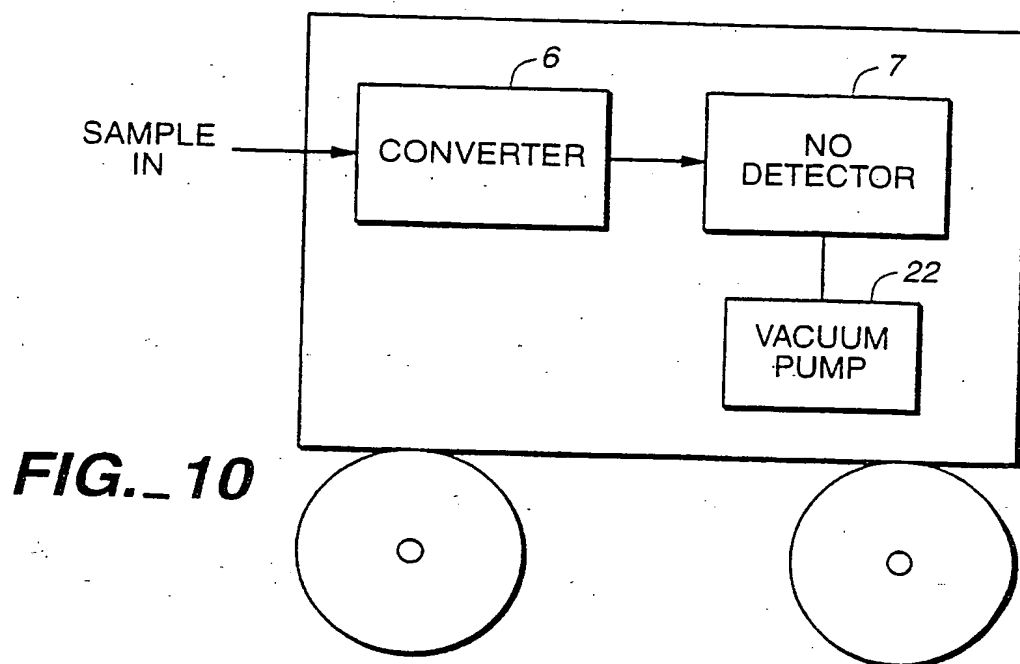
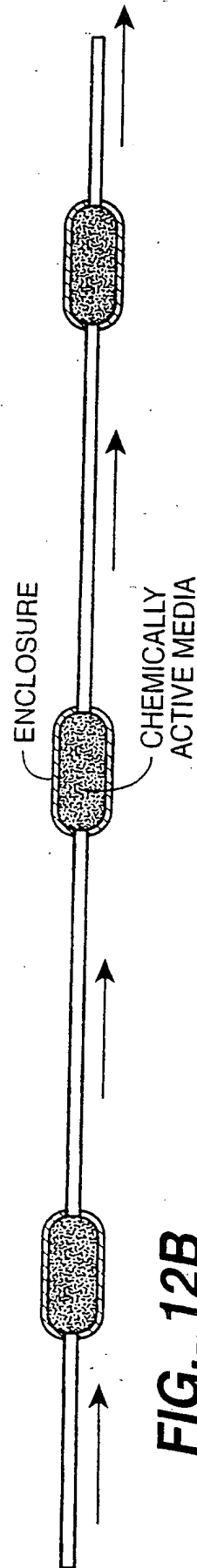
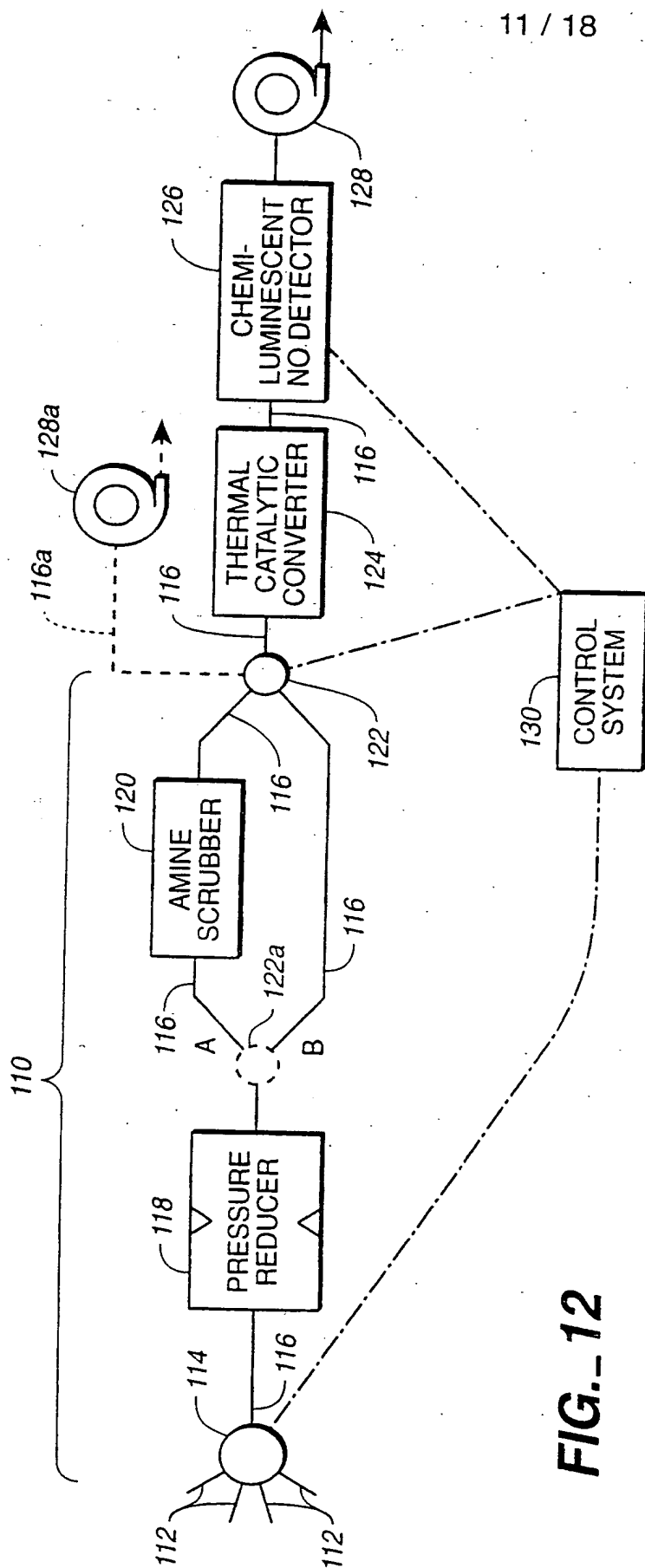


FIG. 12C
SUBSTITUTE SHEET (RULE 26)

11 / 18



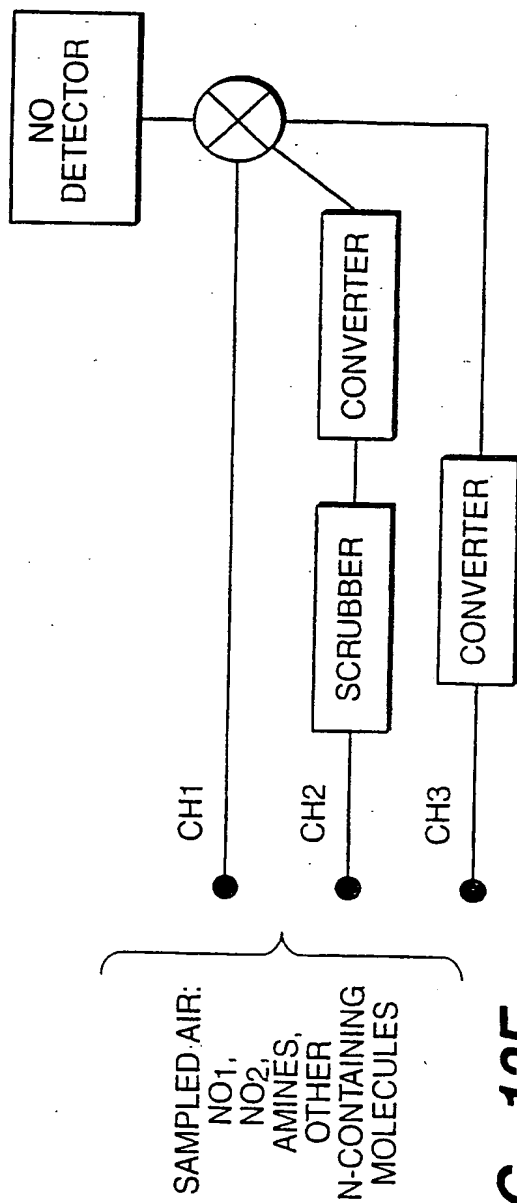


FIG. 12E

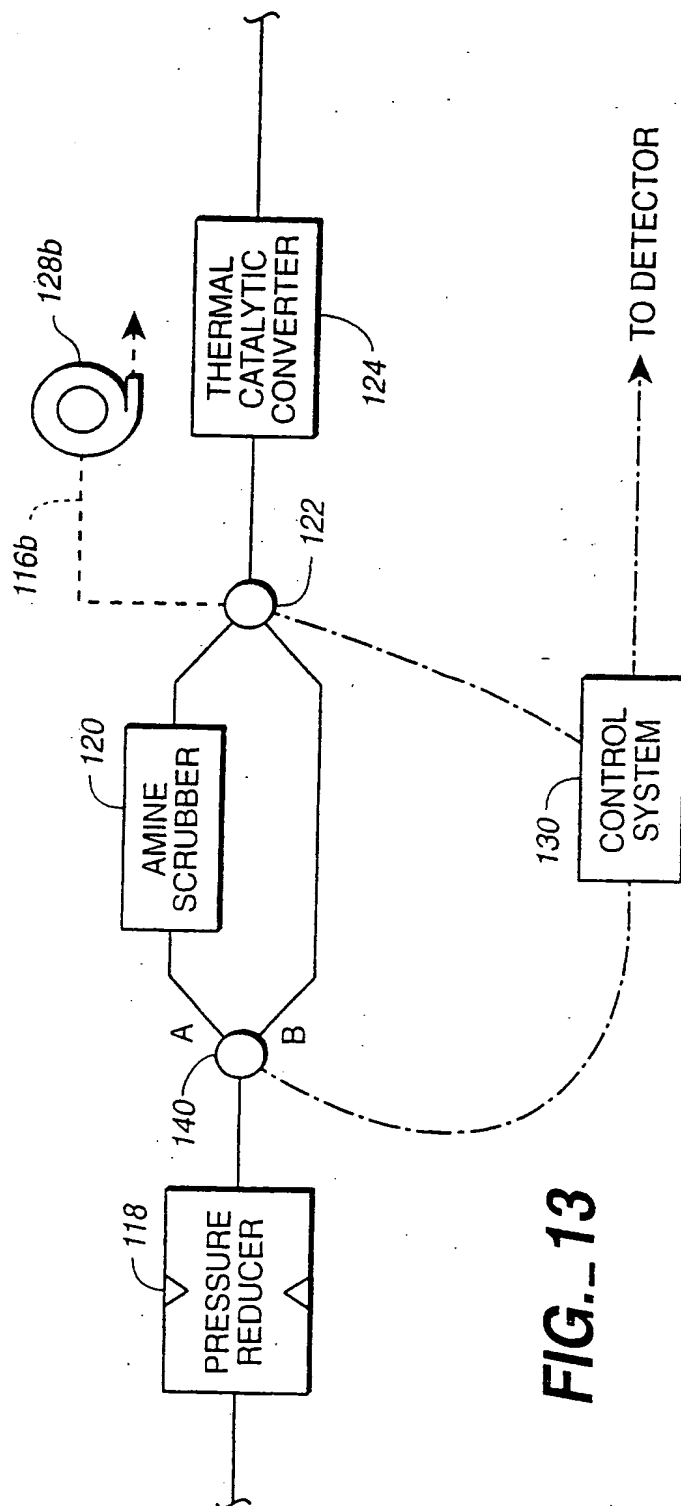


FIG. 13

15 / 18

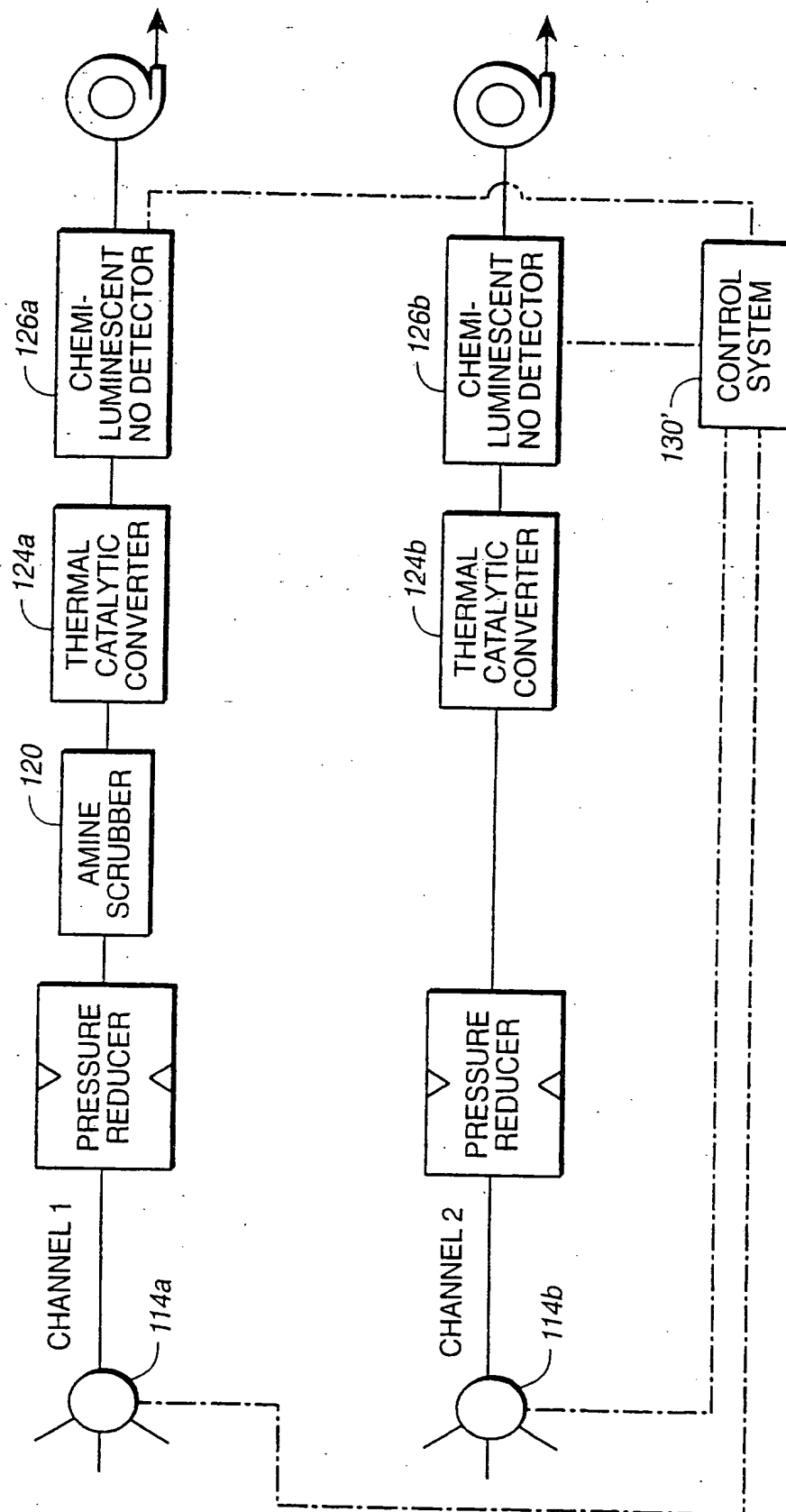


FIG. 16

17 / 18

	CHANNEL	ALARM EVENT FREQUENCY	COST OF ALARM EVENT	NOT OPTIMIZED SAMPLE FREQUENCY	EQUIPMENT COST	ACTUARIAL	SAMPLE FREQUENCY	OPTIMUM SAMPLE
CHAN- NEL	DESCRIP- TION	(EVENTS/ HOUR)	(\$/AVG. ALARM EVENT)	(SAMPLES/ HOUR)	COST/HOUR TO SAMPLE	COST/HOUR TO SAMPLE	INSTRUC- TIONS	FREQUENCY (SAMPLES/ HOUR)
1	STEPPER STAGE	6.00E-03	\$7,000	0.86	\$16	\$84.00	INCREASE FREQUENCY TO	4.43
5	STEPPER INTER- STACK	2.00E-04	\$7,000	0.86	\$16	\$2.80	REDUCE FREQUENCY	0.15
6	TRACK INTER- STACK	2.00E-04	\$7,000	0.86	\$16	\$2.80	REDUCE FREQUENCY	0.15
2	INTER- FACE	6.00E-03	\$7,000	0.86	\$16	\$84.00	INCREASE FREQUENCY TO	4.43
3	TRACK, PRE- EXPOSE	6.00E-03	\$7,000	0.86	\$16	\$84.00	INCREASE FREQUENCY TO	4.43
4	TRACK, POST EXPOSE	6.00E-03	\$7,000	0.86	\$16	\$84.00	INCREASE FREQUENCY TO	4.43
7	PHOTO BAY	1.40E-03	\$2,000	0.86	\$16	\$5.60	REDUCE FREQUENCY	0.30

FIG. 18

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/03998

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G01N33/00 G01N21/76

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 333 735 A (HARDY JAMES E ET AL) 8 June 1982 cited in the application see abstract; figure 1	1, 2, 25, 31, 34, 36
A	US 3 647 387 A (BENSON SIDNEY W ET AL) 7 March 1972 cited in the application see abstract see column 1, line 20 - line 30; figure 1	1, 2, 25, 31, 34, 36
A	US 4 301 114 A (ROUNBEHLER DAVID P ET AL) 17 November 1981 see column 1, line 15 - line 21 see column 7, line 28 - column 8, line 37; figure 4	1, 2, 25, 31, 34, 36

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

2 June 1998

Date of mailing of the international search report

15/06/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Tabellion, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. l. Application No

PCT/US 98/03998

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4333735 A	08-06-1982	NONE	
US 3647387 A	07-03-1972	NONE	
US 4301114 A	17-11-1981	DE 3125535 A GB 2078540 A	19-05-1982 13-01-1982
US 3967933 A	06-07-1976	NONE	
US 5567623 A	22-10-1996	US 5470754 A US 5352611 A AU 6239894 A BR 9405736 A CN 1109167 A EP 0685066 A IL 108714 A NO 953247 A WO 9419679 A US 5561068 A ZA 9401201 A AU 676840 B AU 4382793 A CA 2135877 A CN 1082196 A EP 0643840 A HU 75405 A IL 105813 A JP 7507392 T MX 9303150 A NO 944596 A NZ 253474 A US 5318911 A WO 9324841 A US 5569606 A US 5733783 A US 5688693 A US 5376550 A ZA 9303727 A AU 672011 B AU 4382993 A	28-11-1995 04-10-1994 14-09-1994 05-12-1995 27-09-1995 06-12-1995 31-10-1996 20-10-1995 01-09-1994 01-10-1996 19-09-1994 27-03-1997 30-12-1993 09-12-1993 16-02-1994 22-03-1995 28-05-1997 30-09-1997 10-08-1995 30-06-1994 30-11-1994 26-11-1996 07-06-1994 09-12-1993 29-10-1996 31-03-1998 18-11-1997 27-12-1994 01-03-1994 19-09-1996 30-12-1993